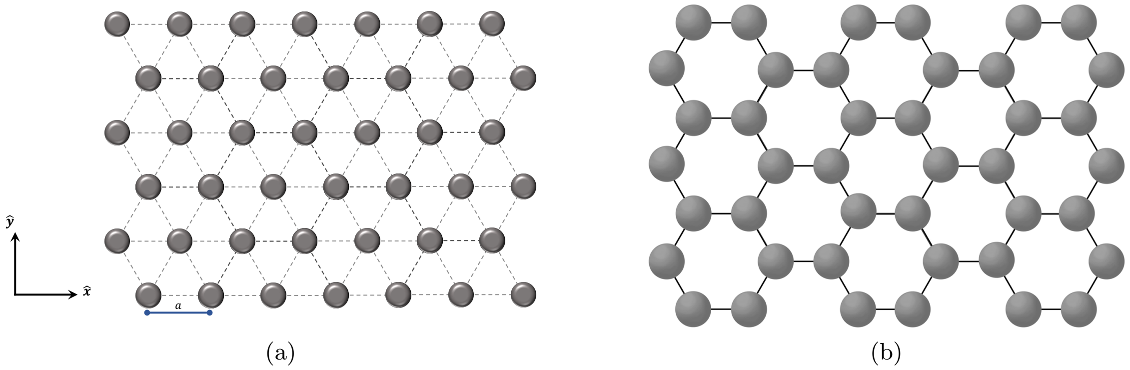
Homework # 9

Exercise 1 - 2D lattices



(a) (b)

Figure 1: (a) Hexagonal lattice; (b) honeycomb structure.

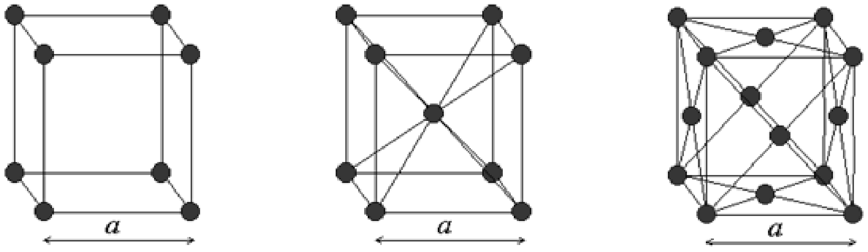
In the last years, two-dimensional materials have drawn a large attention within the framework of electronic and optoelectronic applications, thanks to their peculiar properties. They are just crystalline materials consisting of a single layer of atoms and in many cases they can be obtained with surprisingly simple techniques (*e.g.* exfoliation). To describe the crystal structure of such materials, of course we need two-dimensional lattices. In Fig. 1a we present one of the 5 two-dimensional Bravais lattices, *i.e.* the hexagonal (or triangular) lattice, where a is the lattice parameter, that is the distance between two neighboring atoms.

1. Find a possible choice for the primitive vectors and draw the primitive cell.
2. Draw the Wigner-Seitz cell.
3. Determine the reciprocal lattice, *i.e.* find its primitive vectors. Is the reciprocal lattice a Bravais lattice?
4. Draw the (first) Brillouin zone.

In the hexagonal lattice, if we now remove the atoms at the center of each hexagon, we obtain the honeycomb structure, shown in Fig. 1b, that is the crystal structure of graphene.

5. Is the honeycomb a Bravais lattice?
   (*Hint: remember that a Bravais lattice is an infinite set of discrete points with an arrangement and orientation that appears exactly the same, from whichever of the points the array is viewed.*)
6. Define the crystal structure of graphene (primitive vectors and basis).

Exercise 2 - Cubic lattices



(a) (b) (c)

Figure 2: Cubic crystal systems: (a) simple cubic (SC); (b) body-centered cubic (BCC); (c) face-centered cubic (FCC).

In cubic crystal systems the unit cell is a cube and we can distinguish three different types of cubic structures, shown in Fig. 2. The primitive vectors for these three systems are:

- Simple cubic (**SC**): $\mathbf{a}_1 = a(1,0,0)$, $\mathbf{a}_2 = a(0,1,0)$, $\mathbf{a}_3 = a(0,0,1)$.
- Body-centered cubic (**BCC**): $\mathbf{a}_1 = \frac{a}{2}(-1,1,1)$, $\mathbf{a}_2 = \frac{a}{2}(1,-1,1)$, $\mathbf{a}_3 = \frac{a}{2}(1,1,-1)$.
- Face-centered cubic (**FCC**): $\mathbf{a}_1 = \frac{a}{2}(0,1,1)$, $\mathbf{a}_2 = \frac{a}{2}(1,0,1)$, $\mathbf{a}_3 = \frac{a}{2}(1,1,0)$.

1. Compute the volume of the primitive cell for each lattice. Which is the most packed[1] structure?
   (*Hint: the volume of the primitive cell is* $v = |\mathbf{a}_1 \cdot \mathbf{a}_2 \times \mathbf{a}_3|$.)
2. Determine the primitive reciprocal lattice vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ for these three lattices and the volumes of the corresponding Brillouin zones.
3. For each lattice determine the coordination number, that is the number of first nearest-neighbors to a given atom, and the corresponding distance.

In many simple metals the atoms are arranged in a FCC crystal structure, as for example in aluminum, copper and gold. The lattice constants of these materials are $a_{\mathrm{Al}} = 4.05\,\text{Å}$, $a_{\mathrm{Cu}} = 3.61\,\text{Å}$, and $a_{\mathrm{Au}} = 4.08\,\text{Å}$.

4. Estimate the density (g/cm^3) of aluminum, copper and gold.
   (*Hint: the atomic weight for aluminum is about* $27u$, *for copper* $63.5u$ *and for gold* $197u$. *The atomic mass unit is* $1u \simeq 1.66 \cdot 10^{-27}$ kg.)

---

[1] For most "packed" we mean the most dense structure.

Exercise 3 – Bloch's theorem and plane waves

Let us consider an electron in an external periodic potential $\hat{V}_{ext}$, as it is the case for an electron "travelling" in a crystalline solid. The Hamiltonian operator of this system is

$$\hat{H} = \frac{\hat{\mathbf{p}}^2}{2m} + \hat{V}_{ext}, \tag{1}$$

where the operator $\hat{V}_{ext}$ in the coordinate representation reads:

$$V_{ext}(\mathbf{r}) = V_{ext}(\mathbf{r}+\mathbf{R}), \tag{2}$$

and $\mathbf{R}$ is the Bravais lattice vector.

From Bloch's theorem we know that we can choose the wavefunctions (eigenstates of the Hamiltonian) to be of the form $\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$, where $u_{n\mathbf{k}}(\mathbf{r})$ is a periodic function (with the same periodicity of the crystal and the potential, $u_{n\mathbf{k}}(\mathbf{r}+\mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r})$). In this exercise, we will start to understand how Bloch's theorem and the plane waves expansion help to solve the Schrödinger equation in crystalline materials.

1. Write the Schrödinger equation $\hat{H}\psi_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}\psi_{n\mathbf{k}}(\mathbf{r})$ in terms of the lattice-periodic parts of the wavefunction, i.e. $u_{n\mathbf{k}}(\mathbf{r})$. You should obtain an equation of the form $\hat{H}_{\mathbf{k}}u_{n\mathbf{k}}(\mathbf{r}) = \varepsilon_{n\mathbf{k}}u_{n\mathbf{k}}(\mathbf{r})$. How does $\hat{H}_{\mathbf{k}}$ differ from $\hat{H}$?

The advantage of working with $u_{n\mathbf{k}}(\mathbf{r})$ functions is that they are *lattice-periodic functions* with the periodicity of the Bravais lattice.

2. Write the plane-wave expansion for $u_{n\mathbf{k}}(\mathbf{r})$. For this expansion, is the set of plane waves discrete or continuous?

3. Prove that plane waves are eigenstates of the momentum operator $\hat{\mathbf{p}}$.

In the following, you may find useful to remember that the Fourier transform of a function $f(\mathbf{r})$ can be defined as (V is the volume of the crystal):

$$f(\mathbf{G}) = \frac{1}{V}\int_V f(\mathbf{r})e^{-i\mathbf{G}\cdot\mathbf{r}}d\mathbf{r} \tag{3}$$

4. Write $\varepsilon_{n\mathbf{k}} = \langle u_{n\mathbf{k}}|\hat{H}_{\mathbf{k}}|u_{n\mathbf{k}}\rangle$ using the plane waves expansion for $u_{n\mathbf{k}}(\mathbf{r})$.

   Hint 1: For the Fourier transform of a periodic function use the result of point 2.

   Hint 2: $\frac{1}{V}\int_V e^{i(\mathbf{G}'-\mathbf{G})\cdot\mathbf{r}}\,d\mathbf{r} = \delta_{\mathbf{G},\mathbf{G}'}$.

Suppose we want to describe features of the electronic structure of Aluminum which vary on a length scale of $\delta = 0.1$ a.u., then you need Fourier components at least up to $G_{max} \approx 2\pi/\delta$.

5. Estimate the number of plane waves that you need in order to describe such features of the electronic structure of Aluminium.

   Hint: compute the volume of the Brillouin zone and the volume of the sphere of radius G_{max}.